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Modeling of a severe dust event and its impacts on ozone photochemistry over the downstream Nanjing megacity of eastern China

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HIGHLIGHTS

- The model reproduces the onset time and downstream transport of this dust event.
- Dust particles act as a sink for trace gases through heterogeneous reactions.
- The negative radiation feedback by dust aerosols lead to a small decrease of O_3.

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ABSTRACT

Dust aerosols could affect tropospheric photochemistry by interacting with solar radiation or providing reactive surfaces for heterogeneous reactions. This study examines the effects of a typical springtime dust storm (16–18 March, 2014) on ozone photochemistry over the downstream Nanjing megacity in eastern China. The on-line coupled Weather Research and Forecasting-Chemistry (WRF-Chem) model is used, with the inclusion of eight heterogeneous reactions on dust surfaces. Comparisons with satellite data and visibility record indicate that the model is capable of reproducing the onset time and downstream transport of this dust event. Dust particles act as a sink for all these trace gases examined here. The net decreases of O_3, NO_2, NO_3, N_2O_5, HNO_3, $^{\bullet}OH$, $HO_2^{\bullet}$ and H_2O_2 in the atmosphere are estimated as −6.1%, −16.0%, −37.4%, −13.9%, −47.7%, −6.0%, −9.2% and −29.7%, of which more than 80% can be explained by heterogeneous chemistry on dust surfaces. The decreases in ground photolysis rate and $^{\bullet}OH$ concentration, along with changes in other weather variables induced by dust aerosols (i.e., radiation and temperature) lead to lower photochemical activity and a small decrease of O_3 mixing ratio by roughly 0.5%. This study highlights the importance of dust interaction with ozone photochemistry, and also sets the stage for further investigation of the complicated dust impacts on tropospheric aerosol chemistry.

1. Introduction

Mineral dust generated by wind erosion in arid or semiarid areas is the primary source of natural atmospheric aerosols. Annually, about 500–6,000 Tg of dust particles are emitted into the atmosphere (Ginoux et al., 2001; Zender et al., 2003), which is yet rising as a result of the ongoing land erosion, mining and industrial activities.

Wind-sand disasters have gained wide concerns due to their adverse effects on health (Park et al., 2016), visibility (Kavouras et al., 2009) and biogeochemical cycle (Jickells et al., 2005). Moreover, once in the atmosphere, the mineral dust can be transported long distances from the origin sources (McKendry et al., 2001; Uno et al., 2009). Through long-range dust cycles, these airborne dust particles could interact with atmospheric trace gases through disturbing the earth's radiation budget (Quijano et al., 2000; Sassen, 2002), or providing reactive surfaces for heterogeneous reactions (Bian and Zender, 2003; Kumar et al., 2014; Underwood et al., 2001).

It is well recognized that mineral dust could considerably affect the tropospheric photochemistry through aerosol-radiation effects. Using 1-D radiation transfer models, numerous studies evaluated

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the aerosol effects on photolysis rate and ozone (O_3) productivity in the atmosphere (Dickerson et al., 1997; He and Carmichael, 1999; Jacobson, 1998; Liao et al., 1999); they concluded that absorbing aerosols inhibited photochemical reactions and ozone production by 6–11%, while scattering aerosols accelerated ozone production by 11–18%. More recently, it has been suggested that mineral dust is responsible for 5–20% reduction in the photolysis rates of O_3 and NO_2 throughout the Northern Hemisphere (Martin et al., 2003; Tie et al., 2005; Ying et al., 2011). However, the neglect of aerosol-radiation-chemistry feedback in off-line models is expected to cause noticeable biases in the meteorological and chemical forecasts (Forkel et al., 2012; Kong et al., 2015; Makar et al., 2015a, 2015b). In recent years, new generations of on-line models have been developed and used for Europe and North America. It is found that the interaction between meteorology and chemistry could be significant during strong air pollution episodes such as wild fire or dust events (Chen et al., 2014; Kong et al., 2015; Konovalov et al., 2011; Liu et al., 2016a; Wong et al., 2012).

Otherwise, laboratory and modeling studies showed that heterogeneous reactions on the surfaces of mineral aerosols favored the uptakes of atmospheric trace gases (Bauer et al., 2004; Dentener et al., 1996; Tang et al., 2004; Wang et al., 2012; Zhang and Carmichael, 1999; Zhu et al., 2010). Reactions of O_3, N_2O_5, and HO_2• radical on dust surfaces were found to affect the photochemical oxidant cycle, with O_3 decreased by up to 10% near the source regions (Dentener et al., 1996). The global modeling by Bauer et al. (2004) presented a decrease in tropospheric O_3 by 5% due to the heterogeneous reactions on mineral dust. By far, there have been considerable improvements in the understanding of heterogeneous chemistry. A major advancement is the demonstration of humidity-dependence for the uptake coefficients of some trace gases, e.g., O_3 (Cwiertny et al., 2008), HNO_3 (Liu et al., 2008), •OH (Bedjanian et al., 2013), N_2O_5 (Bauer et al., 2004) and H_2O_2 (Pradhan et al., 2010). The renoxification mechanism of HNO_3 to yield NOx (Rogaski et al., 1997) is ignored in many modeling studies, which has recently been proven to be important in atmospheric photochemistry (Knipping and Dabdub, 2002; Mochida and Finlayson-Pitts, 2000; Rivera-Figueroa et al., 2003; Wang et al., 2012). Thereby, it is essential to reassess the importance of mineral dust in tropospheric photochemistry by including these recent advancements.

East Asia is one of the world's largest dust source regions, accounting for 10–25% of global dust load (Tegen and Schepanski, 2009). During spring and occasionally in winter, dust storms originating in East Asia frequently strike eastern China through long-range transport, causing propagated climatic and environmental influence along the pathways (Gong et al., 2003; Tan et al., 2012). Existing observations identified that Asian dust tended to be more absorbing, with single scattering albedo as low as 0.76 (Costa et al., 2006). Such tremendous dust emissions together with a high absorbing efficiency could significantly perturb the radiative budget and tropospheric chemistry in eastern China (Park et al., 2005). Moreover, heterogeneous chemistry is currently neglected in many regional chemical models because of its large uncertainties. There remains a question as to what extent the mineral dust behaves as an effective surface interacting with trace gases.

Nanjing City, located in the northwest of Yangtze River Delta, is one of the megacities in eastern China. The urban atmosphere in Nanjing was heavily polluted by local emissions and long-distance transport of dust (Huang et al., 2013). This paper examines the impacts of a severe dust event on ozone photochemistry over the downstream Nanjing megacity through direct radiation feedback and heterogeneous process. The on-line coupled Weather Research and Forecasting-Chemistry (WRF-Chem) model is used, with the inclusion of several key heterogeneous reactions on dust surfaces and updated information on uptake coefficients. The model set-up and experimental designs are presented in Sec. 2. Sec. 3 discusses the impacts of dust aerosols on ozone photochemistry. Finally, a summary is presented in Sec. 4.

2. Model setup and experimental designs

2.1. WRF-Chem model descriptions

The WRF-Chem model developed by Grell et al. (2005) represents the state-of-the-science treatments of coupled meteorology/chemistry/aerosol/radiation. WRF-Chem model version 3.7 is used here. It is set up with a four-nested grid system, with horizontal resolutions of 81, 27, 9 and 3 km, and grids of 87 × 74, 84 × 69, 69 × 63 and 54 × 60 (Fig. 1a). The innermost domain focuses on Nanjing. 24 vertical layers are spaced unequally from the ground to 50 hPa.

The initial and boundary meteorological conditions are obtained from the 1° × 1° National Centers for Environmental Prediction global final analysis fields every 6 hours. 12-hour spin-up time is allowed for each 60-hour model cycle to allow for the influence of initial conditions. The static geographical fields, such as land-use type, vegetation fraction and leaf area index, are interpolated from Moderate Resolution Imaging Spectroradiometer land products (Li et al., 2014). The Multi-resolution Emission Inventory for China in 2012 (http://meicmodel.org) is used for the three outer domains. Local anthropogenic emission inventory for the inner domain is developed by Li et al. (2011). Biogenic emissions are calculated online using the Model of Emissions of Gases and Aerosols from Nature (Guenther et al., 2006).

A dust emission scheme developed and validated by Shaw et al. (2008) is used to estimate the dust emissions. The main land-use categories that are identified as potential dust sources are desert, grass and shrub (Fig. 1a). The dust emission flux (F, unit: g cm^{-2} s^{-1}) is calculated as a function of surface wind stress, vegetation type and soil type, as shown in Eq. (1).

$$F = \alpha C u_*^4 \left(1 - \frac{f_w u_{*t}}{u_*}\right) \quad (1)$$

where u_* (cm s^{-1}) is friction velocity; u_{*t} (cm s^{-1}) is the threshold friction velocity below which dust emission does not occur; f_w is a soil moisture factor; α is the vegetation mask from zero to one; C (g cm^{-6} s^3) is an empirical constant.

The Carbon-Bond Mechanism version Z gas-phase chemical mechanism (Zaveri and Peters, 1999) and Model for Simulating Aerosol Interactions and Chemistry (MOSAIC) aerosol module (Zaveri et al., 2008) are used in WRF-Chem. The MOSAIC sectional approach takes into account nine species (sulfate, nitrate, ammonium, organic carbon, black carbon, sodium chloride, calcium carbonate, water and other unspecified inorganic aerosols) distributed into eight size bins from 0.4 to 10 μm in diameter. Mie theory is used to calculate the aerosol optical properties, including extinction efficiency, single scattering albedo and asymmetry factor, based on the aerosol composition, size distribution and mixing state (Barnard et al., 2010). A typical short-wave refractive index for dust particle is assumed as 1.55 + 0.006i based on several models (Dey et al., 2004) and field observations in northern China (Logan et al., 2013; Wu et al., 2009). The long-wave refractive index of dust particle is adopted from the Optical Properties of Aerosols and Clouds dataset (Hess et al., 1998).

The short- and long-wave radiation transfer in the atmosphere is represented by the Rapid Radiative Transfer Model GCM radiation scheme (Gallus and Bresch, 2006). The aerosol radiative effects on photolysis rates are calculated using the Fast-J radiation scheme